Uranium(VI) Sulfilimine Complexes: A New Class of Nitrogen Analogues of the Uranyl Ion

V. Cliff Williams,[†] Matthias Müller,[‡] Michael A. Leech,[‡] Robert G. Denning,*[,†] and Malcolm L. H. Green[†]

Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, U.K., and Chemical Crystallography Laboratory, University of Oxford, 9 Parks Road, Oxford OX1 3PD, U.K.

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The compound tetraphenylphosphonium tetrachlorooxo-*S*,*S*-diphenylsulfiliminatouranium, $[Ph_4P][UOCl_4(NSPh_2)]$, has been prepared in high yield from $[Ph_4P][UOCl_5]$ and $[Ph_2S{=}NSiMe_3]$. An X-ray structure of this compound shows that the uranium atom has a pseudooctahedral geometry with oxygen and nitrogen atoms in trans positions. The structure of the analogous phosphoriminato complex $[Ph_4P][UOCl_4(NPPh_3)]$ has been determined for comparison. Derivatization of the sulfide group shows that only a limited range of functionalization confers stability toward reduction. The emission spectrum of the first electronic excited state reveals a greatly reduced energy compared with that of the uranyl ion. This red shift in the transition is consistent with the weakening of the U−N bond relative to the U−O bond.

Introduction

The chemistry of uranium(VI) is dominated by the uranyl cation UO_2^{2+}, which is exceptionally robust both thermally and chemically.[1] The multiply bonded oxo group is isoelectronic with imido ligands of the type =N−R, where R is usually alkyl or aryl, and much modern coordination chemistry has been developed from this similarity. However, there are few examples of imido ligands bound to uranium(VI), and this remains one of the synthetic goals of actinide chemistry. The failure of the traditional synthetic routes used for transition-metal complexes has been attributed to the highly electropositive nature of uranium.[2] However, during the last 10 years, several successful strategies have been developed.[3−6]

One of the routes used to synthesize uranium−imido type compounds was that of Brown et al., who reacted uranium oxypentachloride $[Ph_4P][UOCl_5]$ with *N*-trimethylsilylphophorimines to yield compounds of the type $[Ph_4P][UOCl_4NPAr_3]$ (Ar = Ph, *m*-MeC_6H_4) in moderate yields.[6,7] This is not a quantitative reaction; side products of the bisphosphorimine $[UCl_4(NPAr_3)_2]$ and uranyl ion $[Ph_4P]_2[UO_2Cl_4]$ could also be isolated, albeit in low yield, ∼10%, and this considerably hampers isolation and purification of the mixtures. Brown also noted that only phosphorimine ligand precursors which bore at least one aromatic ring on the parent phosphine, such as PMe_2Ph, formed stable complexes. For example, the reaction with $Me_3SiNPMe_3$ gave only reduction products such as UCl_6.[2−] In an attempt to expand this chemistry, it was decided to explore the factors that are necessary for stable, isolable compounds to be formed.

Some preliminary studies on the reactions between $[Ph_4P][UOCl_5]$ and the phosphoriminato ligands $Me_3SiNP(Ph)_x(Cl)_{3-x}$, $x = 0, 1, 2$, show that reductive chlorination of the uranium center occurs with almost quantitative production of $[Ph_4P][UCl_6]$.[15] This contrasts with the chemistry of tungsten, where the compounds WCl_4NPCl_3 and $WCl_4(NPPhCl_2)_2$ are stable and crystalline.[8] Thus, attention was turned to ylidic species other than phosphorimines. Holm et al.[9] have presented a comprehensive survey of such types of reagents, many of which exist as the *N*-toslylate derivatives, mainly based upon group 15, but also some from groups 16 and 17. Although many *N*-tosyl ylides are already known in the literature and many may provide suitable ligands, the tosylate function proved incompatible with the highly oxophilic uranium oxopentachloride since oxygen abstraction occurs, yielding the uranyl ion. The trimethylsilyl group overcomes this unwanted side reaction, but restricts the available ligand precursors to those derived from phosphorus and sulfur. In this paper we discuss the reactions of N-trimethylsilylsulfilimines with $[Ph_4P][UOCl_5]$ and investigate the effect of substituents on their stability.

Experimental Section

All preparations were carried out under an atmosphere of pure argon or in an inert-atmosphere box under nitrogen. Standard Schlenk-line techniques were used throughout. All solvents were dried and distilled prior to use, and all chemicals were used as supplied by Aldrich Chemical Co. $Ph_2S{=}NSiMe_3$,[10] $Ph_3P{=}NSiMe_3$,[11] and $[Ph_4P][UOCl_4(NPPh_3)]$[7] were prepared as described in the literature. $(o\text{-}MeC_6H_4)_2S{=}NSiMe_3$, $(p\text{-}ClC_6H_4)_2S{=}NSiMe_3$, and $(C_6D_5)_3PNSiMe_3$ were prepared via similar routes. Infrared spectra were recorded on a 6020 Galaxy series FT-IR instrument. NMR spectra were recorded on a Varian Unity 500 spectrometer, referenced to TMS. Elemental analyses were

* Corresponding author. E-mail: bob.denning@chem.ox.ac.uk.
† Inorganic Chemistry Laboratory.
‡ Chemical Crystallography Laboratory.

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performed by the Microanalytical Department of the Inorganic Chemistry Laboratory in Oxford.

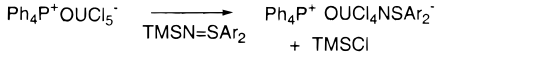
Synthesis of [Ph$_4$P][UOCl$_4$(NSPh$_2$)] (1). To a mixture of [Ph$_4$P][UOCl$_5$] (0.77 g 1.0 mmol) in 20 mL of acetonitrile at 50 °C was added 18 mL of an acetonitrile solution of Ph$_2$S═NSiMe$_3$ (0.27 g 1.0 mmol). The color immediately changed from light orange to deep red. The solution was stirred for 1 h, and then the solvent was evaporated under reduced pressure. The sticky red oil was then extracted into 20 mL of dichloromethane, filtered, and layered with toluene. After 5 days, and decantation of the mother liquor, large red plates could be isolated by hand. Yield: 0.84 g (0.9 mmol, 90%). Anal. Calcd for $C_{36}H_{30}Cl_4NOPSU$: C, 46.2; H, 3.2; N, 1.5; Cl, 15.2; P, 3.3; U, 25.4. Found: C, 45.8; H, 3.0; N, 1.5; Cl, 15.6; P, 3.6; U, 25.3. IR (CsI, cm^{-1}): 3060m, 1590m, 1477m, 1441s, 1109s, 1008vs, 988vs, 845s, 752s, 724s, 692s, 528s. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 7.93 (4H, t, *p*-C_6H_5, Ph$_4$P), 7.78 (8H, m, *m*-C_6H_5, Ph$_4$P), 7.60 (18H, m, C_6H_5). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ = 117.92 (d, J_{C-P} = 90 Hz, P−C_6H_5), 127.18 (s, S−C_6H_5), 130.60 (s, S−C_6H_5), 131.02 (d, J_{C-P} = 12 Hz, P−*o*-C_6H_5), 133.32 (s, S−C_6H_5), 134.86 (d, J_{C-P} = 10 Hz, P−*m*-C_6H_5), 136.09 (s, P−*p*-C_6H_5), 141.19 (s, S−C_6H_5). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2): δ = 22.83 (s, Ph$_4$P).

Synthesis of [Ph$_4$P][UOCl$_4${NS(*p*-ClC$_6$H$_4$)$_2$}] (4). To a mixture of [Ph$_4$P][UOCl$_5$] (1.0 g 1.3 mmol) in 20 mL of dichloromethane at 50 °C was added 20 mL of a dichloromethane solution of (*p*-ClC$_6$H$_4$)$_2$S═NSiMe$_3$ (0.44 g 1.3 mmol). Immediately, the color changed from light orange to deep red. The solution was stirred for 1 h, and then the solvent was evaporated under reduced pressure. The resulting red solid was reextracted into 20 mL of dichloromethane, filtered, and layered with toluene. After 5 days, and decantation of the mother liquor, followed by washing with 2 mL of cold dichloromethane, a dark red microcrystalline solid could be isolated. Yield: 1.2 g (1.2 mmol, 90%). Anal. . Calcd for $C_{36}H_{28}Cl_6NOPSU$: C, 43.0; H, 2.8; N, 1.4; Cl, 21.2; P, 3.1. Found: C, 42.4; H, 2.9; N, 1.4; Cl, 21.1; P, 3.1. IR (CsI, cm^{-1}): 3060m, 1570m,1477m, 1441s, 1109s, 1030vs, 988vs, 842s 752s 724s 692s 526s. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 7.91 (4H, t, *p*-C_6H_5, Ph$_4$P), 7.76 (8H, m, *m*-C_6H_5, Ph$_4$P), 7.60 (16H, m, C_6H_5). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ = 117.49 (d, J_{C-P} = 90 Hz, P−C_6H_5), 128.24 (s, C_6H_4Cl), 130.51 (d, J_{C-P} = 12 Hz, P−*o*-C_6H_5) (s, C_6H_4Cl), 134.44 (d, J_{C-P} = 10 Hz, P−*m*-C_6H_5) 135.67 (s, P− *p*-C_6H_5) 139.22 (s, C_6H_4Cl), 139.60 (s, C_6H_4Cl). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2): δ = 22.83 (s, Ph$_4$P).

Synthesis of [Ph$_4$P][UOCl$_4${NP(C$_6$D$_5$)$_3$}] (5). (C$_6$D$_5$)$_3$PNSiMe$_3$ (0.70 g 2.0 mmol) and [Ph$_4$P] [UOCl$_5$] (1.54 g 2.0 mmol) were mixed in a thick-walled Rotaflo ampule, and dichloromethane (30 mL) was added. The solution was partially evacuated and then heated to 90 °C for 2 h, during which time the color changed from orange to red. Upon cooling, the solution was transferred to a Schlenk tube, filtered (to remove [Ph$_4$P]$_2$[UO$_2$Cl$_4$]), and concentrated. The sample was isolated by crystallization in a solvent bridge from this dichloromethane solution using diethyl ether. Yield: 1.21 g (1.2 mmol, 59%). Anal. . Calcd for $C_{42}H_{20}Cl_4D_{15}NOP_2U$: C, 46.4; H, 3.3; N, 1.3 (Found: C, 46.3; H, 3.3; N, 1.3. IR (CsI, cm^{-1}): 3060m 2279w 1570w 1490w 1436s 1109s 1097vs 1030vs 988vs 863s 760s 726s 692s 530s.^{1}H NMR (500 MHz, CD_2Cl_2): δ = 7.91 (4H, t, *p*-C_6H_5, Ph$_4$P), 7.76 (8H, m, *m*-C_6H_5, Ph$_4$P), 7.60 (8H, m, *o*-C_6H_5). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ = 117.80 (d, J_{C-P} = 90 Hz, C_6H_5), 126.72 (d, J_{C-P} = 90 Hz, C_6D_5), 128.60 (m, *m*-C_6D_5), 129.81 (t, J_{C-D} = 15 Hz, *p*-C_6D_5), 130.95 (d, J_{C-P} = 12 Hz, *o*-C_6H_5), 133.22 (t, J_{C-D} = 15 Hz, *o*-C_6D_5), 134.74 (d, J_{C-P} = 10 Hz, *m*-C_6H_5), 135.98 (s, *p*-C_6H_5). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2): δ = 22.83 (s, Ph$_4$P), −5.0 (s, Ph$_3$P). ^{2}H NMR (76 MHz, CH_2Cl_2): δ = 7.7 (C_6D_5), 7.9 (C_6D_5).

A crystal of compound **1** was cut to a suitable size and then immersed in highly viscous perfluoropolyether, mounted onto a glass fiber, and plunged into a cold stream of nitrogen gas. The data were collected at 150 K on an Enraf-Nonius DIP2020 image plate diffractometer with graphite-monochromated Mo Kα radiation and indexed for a monoclinic unit cell. Corrections for Lorentz and polarization effects, but not for absorption, were performed. The structure was solved using Patterson methods.[12] Full-matrix least-squares refinement was applied. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms could be located without difficulties in difference Fourier maps. The hydrogen atoms were placed geometrically and included in the final refinement with fixed positional and thermal parameters. The refinement was completed using a Chebyshev weighting scheme. All crystallographic calculations were carried out using the CRYSTALS program package[13] and all diagrams through the CAMERON drawing package. The structure of compound **2** was determined similarly.

Scheme 1. Preparative Route to [Ph$_4$P][UOCl$_4$(NSPh$_2$)] (1)



Results and Discussion

[Ph$_4$P][UOCl$_4$(NSPh$_2$)] (**1**) is formed in 90% yield, by the treatment of the compound [Ph$_4$P][UOCl$_5$] with Ph$_2$S═NSiMe$_3$ in dichloromethane (Scheme 1). Compound **1** is highly soluble in polar solvents, such as acetonitrile, forming a dark red-brown solution, which shows no signs of decomposition after heating at 140 °C for 24 h. Besides heat, **1** is also stable to dry air, although contact with moisture yields the yellow uranyl complex [UO$_2$Cl$_4$]$^{2-}$quantitatively. The infrared spectrum of **1** shows a band at 845 cm^{-1} which can be assigned to the antisymmetric O═U═X vibrational mode, which for [UO$_2$Cl$_4$]$^{2-}$ appears at 922 cm^{-1}. A second band at 1008 cm^{-1} can be assigned to the antisymmetric stretch of the U−N−S linkage and is consistent with the assignments for phosphoriminato complexes.[14]

Besides reacting with water, **1** also reacts with hydrogen sulfide to yield the uranyl ion in 50% yield and various intractable uranium−sulfur species, this product mixture presumably being the result of a disproportionation reaction. Compound **1** also displays a strong affinity for oxygen since it will rapidly abstract the oxygen atom from thionyl chloride upon dissolution, whereas the precursor [Ph$_4$P][UOCl$_5$] is isolated from this solvent.[15]

The X-ray structure of compound **1** has been determined. An ORTEP representation of the structure of the anion is presented in Figure 1; the cation is not shown. Selected bond distances and angles are listed in Table 1, and crystallographic details are given in Table 2.

The molecular structure consists of four ion pairs within the unit cell which belongs to the space group $P2_1/n$. The uranium atom has a pseudooctahedral geometry, with four chlorides forming a square plane around the metal center and oxygen and nitrogen groups arranged trans to each other, giving approximate C_{4v} symmetry at the uranium atom. The metal−oxygen bond length of 178.6(3) pm is comparable to that in [UO$_2$Cl$_4$]$^{2-}$ (177.4(4) pm)[16] as are the metal chloride bond lengths (261.61-(8)−262.70(8) pm). The metal−nitrogen bond is 192.0(3) pm and is noticeably longer than the oxygen bond by 7%, but is well within the range of bond lengths reported for uranium(VI) U═N bonds, which for the related linear imido compounds UF-(NR)({Me$_3$Si}$_2$N)$_3$ (R = Ph, SiMe$_3$) are 1.979(8) and 1.854(23) Å, respectively.[3] The O−U−N angle, 178.9(1)°, is essentially linear, underlining the structural similarity to the uranyl ion. The U−N−S linkage is bent, with an angle of 157.5(2)°. This is within the range of angles seen for structures of tungsten

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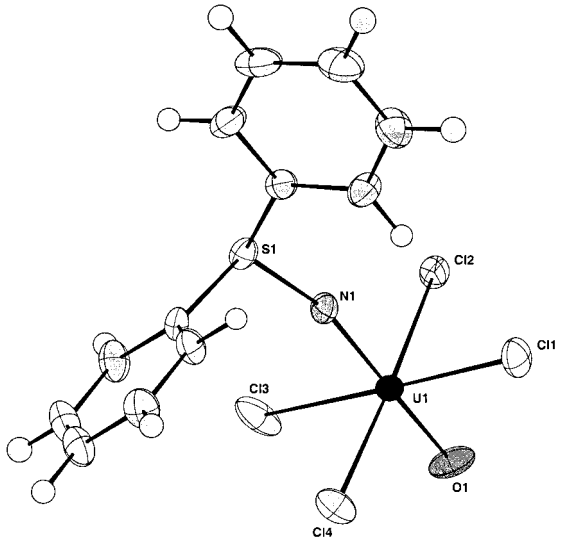

Figure 1. Molecular structure of the anion $[UOCl_4(NSPh_2)]^-$ showing thermal ellipsoids at the 50% probability level.

Table 1. Selected Bond Lengths and Angles for Compounds **1**, $[Ph_4P][UOCl_4(NSPh_2)]$, and **2**, $[Ph_4P][UOCl_4(NPPh_3)]$

bond lengths (Å)			bond angles (deg)		
	1	**2**		**1**	**2**
U−O	1.786(3)	1.777(3)	U−N−P		166.3(2)
U−N	1.920(3)	1.912(3)	U−N−S	157.5(2)	
U−$Cl_{1,2,3,4}$	2.6240(7)	2.6246(9)	N−U−$Cl_{1,2,3,4}$	89.32(9)	90.04(9)
	2.6161(8)	2.6375(9)		89.43(9)	89.94(9)
	2.6174(8)	2.6450(9)		88.5(1)	89.21(9)
	2.6270(8)	2.6216(9)		90.16(9)	89.43(9)
N−S	1.607(3)		O−U−N	178.9(1)	178.7(1)
N−P		1.609(3)			

sulfiliminato complexes. For example, $WF_4(NSPh_2)_2$ has two different angles of 138° and 171°, implying that this angle is highly sensitive to bonding within the molecule and/or crystal packing forces.[17]

The X-ray structure of the compound $[Ph_4P][UOCl_4(NPPh_3)]$ (**2**) is shown in Figure 2, for comparison to that of compound **1**. The counterion and solvent of crystallization (CH_2Cl_2) have been omitted for clarity. Selected bond lengths are given in Table 1 alongside those for compound **1**, and other details are listed in Table 2. Compound **2** was synthesized using the published procedure.[7]

$[Ph_4P][UOCl_4(NPPh_3)]$ crystallizes in the monoclinic space-group $P2_1/c$. The uranium atom is surrounded by four chlorides, forming a square plane, and an oxygen and a nitrogen atom disposed in a trans configuration. The O−U−N angle is 178.7-(1)°, which again demonstrates the strong preference of uranium for a linear bonding arrangement to π ligands. The U−O bond is 177.7(3) pm, the same length as for **1**, which is toward the longer end of the range expected for uranyl U−O distances, in agreement with the band in the infrared spectrum assigned to the O−U−N antisymmetric stretch at 863 cm^{-1}. Likewise, the U−N bond at 191.2(3) pm is identical to that seen for compound **1**. All other bonds are typical of those in related structures.

Encouraged by the facile synthesis of compound **1**, it was decided to explore whether other groups instead of phenyl could give rise to uranyl anions with sulfilimine ligands. According to Yoshimura et al. the intermediate sulfilimine $R_2S{=}NH$, from which the ligand precursor is derived, is only stable to hydrolysis and heat if both the R groups are aromatic.[18] Although mixed aryl−alkyl sulfilimines can be isolated, the extended reflux to form the required *N*-trimethylsilylsulfilimine would exclude the isolation of the ligand precursor. It was therefore decided to form the *o*-tolyl derivative because this allowed for potentially increased solubility of the final product. Treatment of $[Ph_4P][UOCl_5]$ with 1 equiv of $(o\text{-}MeC_6H_4)_2S{=}NSiMe_3$ under the same conditions as previously used leads to the formation of a yellow-green solution. The solution consists of nearly equal proportions of $UO_2Cl_4^{2-}$ and UCl_6^{2-} (by infrared and Raman spectroscopy), the presence of which can be explained by a

Table 2. Crystallographic Data for Compounds **1**, $[Ph_4P][UOCl_4(NSPh_2)]$, and **2**, $[Ph_4P][UOCl_4(NPPh_3)]$

	1	**2**
chemical formula	$[Ph_4P][UOCl_4(NSPh_2)]$	$[Ph_4P][UOCl_4(NPPh_3)]$
empirical formula	$C_{36}H_{30}U_1O_1N_1S_1P_1Cl_4$	$C_{43}H_{37}U_1O_1N_1P_2Cl_6$
fw	935.52	1096.47
temp (K)	150	150
wavelength (Å)	0.710 70 Å	0.710 70
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
unit cell dimens	$a = 14.414$ Å	$a = 10.542(1)$ Å
	$b = 15.912$ Å	$b = 13.632(1)$ Å
	$c = 15.948$ Å	$c = 30.362(1)$ Å
	$\beta = 99.46°$	$\beta = 94.101(2)°$
V (Å^3)	3607.96	4352.24
Z	4	4
density (calcd) (Mg/m^3)	1.72	1.67
Abs coeff (mm^{-1})	4.69	4.01
F(000)	1768.29	2097.75
cryst size (mm^3	0.28 × 0.28 × 0.16	0.30 × 0.20 × 0.20
θ range	1.49 to 26.5°	1.49 to 26.63°
index ranges	$-18 \le h \le 18$	$-13 \le h \le 13$
	$-18 \le k \le 18$	$-15 \le k \le 15$
	$-19 \le l \le 19$	$-38 \le l \le 38$
no. of reflns collected	42 264	23 463
no. of independent reflns	7023 [R(int) = 0.038]	8274 [R(int) = 0.028]
abs correction	none	none
no. of data/no. of param	6299/526	6438/488
goodness-of-fit on F	0.9197	1.0912
R^a[I > 2σ(I)]	0.0229	0.0253
$R_w{}^b$ [I > 2σ(I)]	0.0329	0.0310
extinction coeff	13.3(55)	40.6(48)
residual density (e•Å^{-3})	0.45 and −0.60	0.78 and −1.48

^{a} $R = [\Sigma(|F_o| - |F_c|)/\Sigma|F_o|]$. ^{b} $R_w = [\Sigma w(F_o^2 - F_c^2)/\Sigma w(F_o^2)^2]^{1/2}$

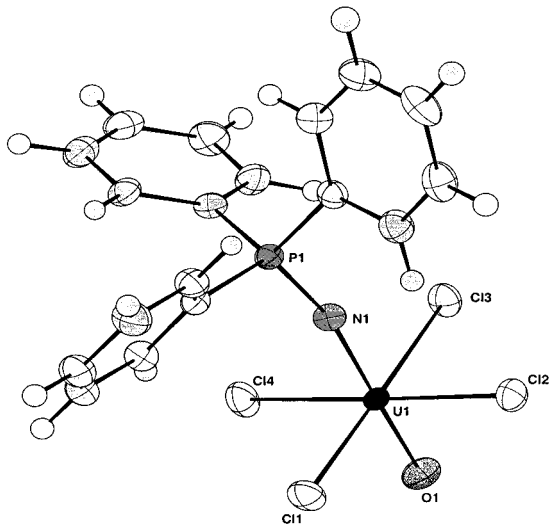

Figure 2. Molecular structure of the anion $[UOCl_4(NPPh_3)]^-$ showing thermal ellipsoids at the 50% probability level.

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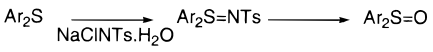
Scheme 2. Formation and Further Reaction of *N*-Tosylsulfilimines



reduction of $[UOCl_5]^-$, followed by disproportionation of the $[UOCl_5]^{2-}$ ion. The fact that the desired molecule $[Ph_4P][UOCl_4\{NS(o\text{-}MeC_6H_4)_2\}]$ (**3**) appears not to be stable is surprising. Since the increase in steric bulk of the phenyl groups is negligible, we attribute the apparent instability of **3** to the electronic influence of the *o*-tolyl groups on the redox properties of the ligand.

To explore this hypothesis, an analogous compound was synthesized with electron-withdrawing groups on the phenyl rings. A *p*-chloro group was chosen because it can be easily introduced, does not contain an oxygen atom (which would otherwise be abstracted by $[UOCl_5]^-$), and does not change any steric requirements. Reaction between $[Ph_4P][UOCl_5]$ and $(p\text{-}C_6H_4Cl)_2S{=}NSiMe_3$ at 50 °C yielded a color change to brown. Isolation provided the compound $[Ph_4P][UOCl_4\{NS(p\text{-}ClC_6H_4)_2\}]$ **4** in 90% yield. Compound **4** is highly thermally stable, being unchanged after 24 h at 150 °C. The infrared data show a strong band at 842 cm^{-1} which is at a lower frequency than in compound **1** (857 cm^{-1}), indicating a weakening of the O−U−N linkage, which is in accord with electron withdrawal from the U−N−S bonds.

The important influence displayed by the aromatic groups can be best understood by considering the inductive effect of the sulfur atom.

In simple valence bond terms, there is a positive charge on the sulfur atom, since it is ylidic. The magnitude of the charge will depend on the electronic properties of the nitrogen and those of the aromatic rings. The other important point to note is that the uranium is a very strong oxidizing agent; i.e., it has a low-lying empty orbital available. Thus, the electrons held in p-π orbitals on the nitrogen can be delocalized between the sulfur orbitals and the vacant uranium orbitals. If, as in the case of the *o*-tolyl-derived ligand, the electron density is increased at the sulfur sufficiently so that the balance of electron density is shifted toward the uranium beyond a certain limit, then spontaneous uranium reduction will occur.

So the question arises whether you can stabilize this type of complex further by the addition of extra electron-withdrawing ligands? Unfortunately this question cannot be answered readily, because it appears that such compounds cannot be prepared, at least by these methods. The synthetic limit occurs for the synthesis of the sulfilimine ligand precursors. The parent sulfide is oxidized with chloramine-T, ($TsNNaCl{\cdot}H_2O$) in methanol solution (Scheme 2). The major side reaction that occurs is the formation of the sulfoxide, presumably by the hydrolysis of the *N*-tosylsulfilimine being produced.[19] As extra electron-withdrawing groups are added to the phenyl rings, the greater is the proportion of the sulfoxide formed, to the point that the *p*-chlorophenyl ligand (as used here) cannot be formed in greater than 10% yield.

In contrast to common uranyl compounds, which are usually bright yellow, the nitrogen analogues synthesized here are a deep red color. This is due to the red shift in the absorption spectrum. The optical transitions of the UO_2^{2+} ion in this region have been much studied and are well understood.[20,21] For the uranyl ion, the emission corresponds to a parity forbidden metal to ligand charge-transfer transition from a nonbonding 5f uranium based LUMO to a mainly oxygen $2p_z$ based ligand HOMO. The transition is centered near 550 nm and is partially allowed due to vibronic coupling. Considerable vibrational fine structure is resolvable at low temperatures. It has a lifetime that can be measured in tens of milliseconds. The emission spectrum of compound **1** proved difficult to detect, being many orders of magnitude less intense than that observed for the uranyl ion. Nonradiative relaxation pathways can be made less effective by removing the highest frequency modes, i.e., C−H stretches. Of all the compounds synthetically accessible, the least difficult to perdeuterate was compound **2.** Thus, $[Ph_4P][UOCl_4(NP(C_6D_5)_3)]$ (**5**) was synthesized, as a dark red microcrystalline solid, in 50% yield, based on the basis of triphenylphosphine-d_{15}.

The low temperature (12 K) emission spectrum of compound **5** shows a broad band centered at 720 nm, of low intensity relative to the uranyl ion, but considerably more intense than for either compound **1** or compound **2**. The lifetime of the emission had also increased. However, there was no resolvable vibrational fine structure, in contrast to the clear progression in the U−O stretching mode that is observed in the UO_2^{2+} emission. This observation is consistent with the HOMO being largely localized on the phosphoriminato donor (vide infra). The electronic excitation from this orbital might be expected to excite a large number of low-frequency internal vibrational modes, as well as deformations in the rest of the ligand. Thus, the emission spectrum will be broadened by the simultaneous creation of a variety of vibrational modes within the ligand, and no clear progressions in any single mode, such as a U−N stretch, would be discernible.

These findings are in good agreement with those of Heinemann et al., who report the experimental bond dissociation enthalpies of the U−O and U−N bonds as 739 ± 164 and 429 ± 122 kJ mol^{-1}, respectively, in the gas-phase $O{=}U{=}N^+$ ion.[22,23] From theoretical calculations, they showed that the HOMO should be mainly localized on nitrogen (35% N $2p_z$ and 1% O $2p_z$) and that it would be raised in energy relative to to that found in the uranyl ion (a result expected purely on the basis of electronegativity arguements). This is tantamount to a reduced HOMO−LUMO energy difference, and is consistent with the 0.5 eV shift in the transition energy, along with the broad and unstructured nature of the emission observed here.

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Supporting Information Available: Full listings of crystallographic data in CIF format, including positions and bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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